

THE CLAIMS

What is claimed is:

1. A method for forming a polymeric hollow fiber, comprising the steps of:
 - (a) providing a solid core fiber;
 - (b) coating at least one layer of a removable substrate material over said solid core fiber;
 - (c) coating at least one layer of a polymeric membrane-forming material over said removable substrate material layer;
 - (d) treating said polymeric membrane-forming material layer to form a solidified polymeric membrane; and
 - (e) removing the removable substrate material layer and the solid core fiber from the solidified polymeric membrane, to form a polymeric hollow fiber comprising a tubular membrane wall enclosing an elongated lumen therein.
2. The method of claim 1, wherein said removable substrate material comprises material selected from the group consisting of sublimable materials, meltable materials, and soluble materials.
3. The method of claim 1, wherein said removable substrate material comprises soluble material selected from the group consisting of acid-soluble materials, alkali-soluble materials, organic-solvent-soluble materials, and water-soluble materials.
4. The method of claim 1, wherein said removable substrate material comprises water-soluble polymeric material selected from the group consisting of polyvinyl pyrrolidones (PVP), polyvinyl alcohols (PVA), and polyethylene glycols (PEG).

5. The method of claim 1, wherein said solid core fiber comprises material selected from the group consisting of metals, metal alloys, glass, ceramics, carbons, polymers, and mixtures thereof.
6. The method of claim 1, wherein said solid core fiber has a cross-sectional outer diameter in a range of from about 10 microns to about 10 millimeter.
7. The method of claim 1, wherein said polymeric membrane-forming material comprises polymeric material selected from the group consisting of polysulfone, polypropylene, polyacrylonitrile, polytetrafluoroethylene, polyethylene, polyvinylidene fluoride, polyamide, polyethyl methacrylate, regenerated cellulose acetate, cellulose triacetate, and mixtures thereof.
8. The method of claim 1, wherein said polymeric membrane-forming material comprises ion-exchange polymeric material selected from the group consisting of perfluorocarbon-sulfonic-acid-based polymers, polysulfone-based polymers, perfluorocarboxylic-acid-based polymers, styrene-vinyl-benzene-sulfonic-acid-based polymers, styrene-butadiene-based polymers, and mixtures thereof.
9. The method of claim 1, wherein said polymeric membrane-forming material comprises perfluorosulfonate ionomer.
10. The method of claim 9, wherein said perfluorosulfonate ionomer is solution extruded over said removable substrate material layer.
11. The method of claim 10, wherein the treatment of said perfluorosulfonate ionomer comprises the steps of: (i) drying said perfluorosulfonate ionomer at a first elevated temperature; and (ii) curing said perfluorosulfonate ionomer at a second elevated temperature.

12. The method of claim 11, wherein the first elevated temperature is in a range of from about 25°C to about 100°C.
13. The method of claim 11, wherein the second elevated temperature is in a range of from about 110°C to about 250°C.
14. The method of claim 1, wherein one or more reinforcing fibers are incorporated into said at least one polymeric membrane-forming material layer to form a fiber-reinforced polymeric membrane.
15. The method of claim 14 wherein the solid core fiber has a longitudinal axis, and wherein said reinforcing fibers extend continuously along the longitudinal axis of said solid core fiber.
16. The method of claim 14 wherein said reinforcing fibers comprises fibers selected from the group consisting of fiberglass, carbon fibers, metal fibers, resin fibers, and composite fibers.
17. The method of claim 14, wherein said reinforcing fibers comprises fiberglass yarns.
18. The method of claim 17, wherein said fiber glass yarns are characterized by an average outer diameter in a range of from about 0.1µm to about 500µm.
19. The method of claim 14, wherein said reinforcing fibers are co-extruded with said polymeric membrane-forming material layer.

20. The method of claim 14, wherein two layers of polymeric membrane-forming material are coated over said removable substrate material layer, and wherein said reinforcing fibers are encapsulated between said two polymeric membrane-forming material layers.
21. The method of claim 1, further comprising the step of providing a removal interface in contact with at least a portion of the removable substrate material layer, to facilitate removal of said removable substrate material.
22. The method of claim 21, wherein said removal interface comprises an open cavity, through which a removing fluid can be passed through to remove said removable substrate material.
23. A method for forming a polymeric hollow fiber, comprising the steps of:
- (a) providing a solid core fiber comprising removable substrate material;
 - (b) coating at least one layer of polymeric membrane-forming material over said solid core fiber;
 - (c) treating said polymeric membrane-forming material layer to form a solidified polymeric membrane; and
 - (d) removing the solid core fiber from the solidified polymeric membrane, to form a polymeric hollow fiber comprising a tubular membrane wall enclosing an elongated lumen therein.
24. The method of claim 23, wherein said removable substrate material comprises material selected from the group consisting of sublimable materials, meltable materials, and soluble materials.

25. The method of claim 23, wherein said removable substrate material comprises soluble material selected from the group consisting of acid-soluble materials, alkali-soluble materials, organic-solvent-soluble materials, and water-soluble materials.
26. The method of claim 23, wherein said removable substrate material comprises water-soluble polymeric material selected from the group consisting of polyvinyl pyrrolidones (PVP), polyvinyl alcohols (PVA), and polyethylene glycols (PEG).
27. The method of claim 23, wherein said solid core fiber has a cross-sectional outer diameter in a range of from about 10 microns to about 10 millimeter.
28. The method of claim 23, wherein said polymeric membrane-forming material comprises polymeric material selected from the group consisting of polysulfone, polypropylene, polyacrylonitrile, polytetrafluoroethylene, polyethylene, polyvinylidene fluoride, polyamide, polyethyl methacrylate, regenerated cellulose acetate, cellulose triacetate, and mixtures thereof.
29. The method of claim 23, wherein said polymeric membrane-forming material comprises ion-exchange polymeric material selected from the group consisting of perfluorocarbon-sulfonic-acid-based polymers, polysulfone-based polymers, perfluorocarboxylic-acid-based polymers, styrene-vinylbenzene-sulfonic-acid-based polymers, styrene-butadiene-based polymers, and mixtures thereof.
30. The method of claim 23, wherein said polymeric membrane-forming material comprises perfluorosulfonate ionomer.

31. The method of claim 30, wherein said perfluorosulfonate ionomer is solution extruded over said removable substrate material layer.
32. The method of claim 31, wherein the treatment of said perfluorosulfonate ionomer comprises the steps of: (i) drying said perfluorosulfonate ionomer at a first elevated temperature; and (ii) curing said perfluorosulfonate ionomer at a second elevated temperature.
33. The method of claim 32, wherein the first elevated temperature is in a range of from about 25°C to about 100°C.
34. The method of claim 32, wherein the second elevated temperature is in a range of from about 110°C to about 250°C.
35. The method of claim 23, wherein one or more reinforcing fibers are incorporated into said at least one polymeric membrane-forming material layer to form a fiber-reinforced polymeric membrane.
36. The method of claim 35, wherein the solid core fiber has a longitudinal axis, and wherein said reinforcing fibers extend continuously along the longitudinal axis of said solid core fiber.
37. The method of claim 35, wherein said reinforcing fibers comprises fibers selected from the group consisting of fiberglass, carbon fibers, metal fibers, resin fibers, and composite fibers.
38. The method of claim 35, wherein said reinforcing fibers comprises fiberglass yarns.

39. The method of claim 38, wherein said fiberglass yarns are characterized by an average outer diameter in a range of from about 0.1 μ m to about 500 μ m.
40. The method of claim 35, wherein said reinforcing fibers are co-extruded with said polymeric membrane-forming material layer.
41. The method of claim 35, wherein two layers of polymeric membrane-forming material are coated over said solid core fiber, and wherein said reinforcing fibers are encapsulated between said two polymeric membrane-forming material layers.
42. The method of claim 23, further comprising the step of providing a removal interface in contact with at least a portion of said solid core fiber, to facilitate removal thereof.
43. The method of claim 42, wherein said removal interface comprises an open cavity inside the solid core fiber, for passing a removing fluid therethrough to remove the solid core fiber.
44. A method for forming a polymeric hollow fiber, comprising the steps of:
- (a) providing a solid core fiber;
 - (b) coating at least one layer of swellable polymeric membrane-forming material over said solid core fiber;
 - (c) treating said swellable polymeric membrane-forming material layer to form a solidified polymeric membrane;
 - (d) contacting said solidified polymeric membrane with a swelling agent to effectuate expansion and disengagement of such polymeric membrane from the solid core fiber; and

(e) removing the solid core fiber from the disengaged solidified polymeric membrane, to form a polymeric hollow fiber comprising a tubular membrane wall enclosing an elongated lumen therein.

45. The method of claim 44, wherein said solid core fiber comprises material selected from the group consisting of metals, metal alloys, glass, ceramics, carbons, polymers, and mixtures thereof.

46. The method of claim 44, wherein said solid core fiber has a cross-sectional outer diameter in a range of from about 10 microns to about 10 millimeter.

47. The method of claim 44, wherein said swellable polymeric membrane-forming material comprises ion-exchange polymeric material selected from the group consisting of perfluorocarbon-sulfonic-acid-based polymers, polysulfone-based polymers, perfluorocarboxylic-acid-based polymers, styrene-vinyl-benzene-sulfonic-acid-based polymers, styrene-butadiene-based polymers, and mixtures thereof.

48. The method of claim 44, wherein said swelling agent comprises water or an organic solvent.

49. The method of claim 44, wherein polymeric membrane-forming material comprises perfluorosulfonate ionomer, and wherein said swellable agent comprises water.

50. The method of claim 44, wherein one or more reinforcing fibers are incorporated into said at least one swellable polymeric membrane-forming material layer to form a fiber-reinforced polymeric membrane.

51. The method of claim 50, wherein the solid core fiber has a longitudinal axis, and wherein said reinforcing fibers extend continuously along the longitudinal axis of said solid core fiber.
52. The method of claim 50, wherein said reinforcing fibers comprises fibers selected from the group consisting of fiberglass, carbon fibers, metal fibers, resin fibers, and composite fibers.
53. The method of claim 50, wherein said reinforcing fibers comprises fiberglass yarns having an average outer diameter in a range of from about 0.1 μ m to about 500 μ m.
54. The method of claim 50, wherein said reinforcing fibers are co-extruded with said swellable polymeric membrane-forming material layer.
55. The method of claim 50, wherein two layers of swellable polymeric membrane-forming material are coated over said solid core fiber, and wherein said reinforcing fibers are encapsulated between said two swellable polymeric membrane-forming material layers.
56. A method for forming an ion-exchange polymeric hollow fiber, comprising the steps of:
- (a) providing a solid core fiber that is subsequently and selectively removable;
 - (b) coating at least one layer of ion-exchange polymeric membrane-forming material over the solid core fiber;
 - (c) treating such ion-exchange polymeric membrane-forming material layer to form a solidified ion-exchange polymeric membrane; and
 - (d) removing the solid core fiber from the solidified ion-exchange polymeric membrane, so as to form an ion-exchange polymeric hollow fiber having a tubular membrane wall enclosing an elongated lumen therein.

57. The method of claim 56, wherein said solid core fiber comprises removable substrate material.
58. The method of claim 56, wherein said solid core fiber is coated with removable substrate material.
59. The method of claim 56, wherein the ion-exchange polymeric membrane-forming material comprises material selected from the group consisting of perfluorocarbon-sulfonic-acid-based polymers, polysulfone-based polymers, perfluorocarboxylic-acid-based polymers, styrene-vinyl-benzene-sulfonic-acid-based polymers, styrene-butadiene-based polymers, and mixtures thereof.
60. The method of claim 56, wherein one or more reinforcing fibers are incorporated into said at least one ion-exchange polymeric membrane-forming material layer to form a fiber-reinforced ion-exchange polymeric membrane.
61. The method of claim 60, wherein the solid core fiber has a longitudinal axis, and wherein said reinforcing fibers extend continuously along the longitudinal axis of said solid core fiber.
62. The method of claim 60, wherein said reinforcing fibers comprises fibers selected from the group consisting of fiberglass, carbon fibers, metal fibers, resin fibers, and composite fibers.
63. The method of claim 60, wherein said reinforcing fibers comprises fiberglass yarns having an average outer diameter in a range of from about 0.1 μ m to about 500 μ m.

64. The method of claim 60, wherein said reinforcing fibers are co-extruded with said ion-exchange polymeric membrane-forming material layer.
65. The method of claim 60, wherein two layers of ion-exchange polymeric membrane-forming material are coated over said solid core fiber, and wherein said reinforcing fibers are encapsulated between said two ion-exchange polymeric membrane-forming material layers.
66. A method for forming a polymeric hollow fiber, comprising the steps of:
- (a) providing a solid core fiber that is subsequently and selectively removable;
 - (b) coating at least one layer of a mixture over the solid core fiber, wherein said mixture comprises polymeric membrane-forming material and removable pore-forming material;
 - (c) treating such mixture layer to form a solidified membrane structure; and
 - (d) removing the solid core fiber from the solidified membrane structure; and
 - (e) removing the pore-forming material from the solidified membrane structure, to form a polymeric hollow fiber having a porous tubular membrane wall enclosing an elongated lumen therein,
- wherein steps (d) and (e) is carried out either simultaneously, or sequentially in any order.
67. The method of claim 66, wherein said solid core fiber comprises removable substrate material.
68. The method of claim 67, wherein the removable substrate material is essentially the same as the removable pore-forming material, and wherein removal of the solid core fiber is carried out simultaneously with removal of the pore-forming material.
69. A polymeric hollow fiber precursor, comprising:

- (a) a solid core fiber comprising at least one removable substrate material; and
- (b) a layer of polymeric membrane-forming material coated over said solid core fiber, wherein said solid core fiber is subsequently and selectively removable for forming a polymeric hollow fiber comprising a tubular polymeric membrane enclosing an elongated lumen therein.

70. A polymeric hollow fiber precursor, comprising:

- (a) a solid core fiber;
- (b) a layer of removable substrate material coated over said solid core fiber; and
- (b) a layer of polymeric membrane-forming material coated over said removable substrate material layer, wherein said solid core fiber and said removable substrate material layer are subsequently removable for forming a polymeric hollow fiber comprising a tubular polymeric membrane enclosing an elongated lumen therein.

71. A method for forming a fiber-reinforced polymeric hollow fibrous membrane, comprising the steps of:

- (a) providing a solid core fiber that is subsequently and selectively removable, wherein said solid core fiber has a longitudinal axis;
- (b) forming one or more layers of polymeric membrane-forming material over the solid core fiber, wherein said polymeric membrane-forming material layers contain one or more reinforcing fibers extending continuously along the longitudinal axis of the solid core fiber;
- (c) treating said one or more polymeric membrane-forming material layers to form a solidified fiber-reinforced polymeric membrane; and

(d) removing the solid core fiber from said polymeric membrane, so as to form a fiber-reinforced polymeric hollow fiber having a tubular membrane wall enclosing an elongated lumen therein.

72. A polymeric hollow fiber precursor, comprising:

- (a) a solid core fiber having a longitudinal axis; and
- (b) one or more layers of polymeric membrane-forming material coated over said solid core fiber,

wherein said one or more polymeric membrane-forming material layers contain one or more reinforcing fibers extending continuously along the longitudinal axis of the solid core fiber, and wherein said solid core fiber is subsequently and selectively removable for forming a fiber-reinforced polymeric hollow fiber comprising a tubular polymeric membrane enclosing an elongated lumen therein.

73. A method for forming a polymeric hollow fiber, comprising the steps of:

- (a) providing a molten removable substrate material;
- (b) providing a viscous solution of polymeric membrane-forming material;
- (c) co-extruding the molten removable substrate material and the viscous solution of the polymeric membrane-forming material, to form a fibrous structure comprising a fibrous core enclosed by a membrane wall, wherein said fibrous core is formed by the molten removable substrate material, and wherein said membrane wall is formed by the viscous solution of the polymeric membrane-forming material;
- (d) cooling the fibrous structure to solidify said fibrous core;
- (e) subsequently, treating the fibrous structure to solidify the membrane wall; and

(f) removing the fibrous core from the solidified membrane wall, forming a polymeric hollow fiber having a tubular membrane wall enclosing an elongated lumen therein.

74. The method of claim 73, wherein said polymeric membrane-forming material comprises ion-exchange polymeric material.

75. A method for forming a polymeric hollow fiber, comprising the steps of:

- (a) providing a molten removable substrate material;
- (b) providing a viscous solution comprising a mixture of polymeric membrane-forming material with removable pore-forming material;
- (c) co-extruding the molten removable substrate material and the viscous solution, to form a fibrous structure comprising a fibrous core enclosed by a membrane wall, wherein such fibrous core is formed by the molten removable substrate material, and wherein such membrane wall is formed by the viscous solution of the mixture;
- (d) cooling the fibrous structure to solidify the fibrous core;
- (e) treating the fibrous structure with coagulating agent, to solidify the membrane wall and concurrently remove the pore-forming material from said membrane wall, forming a solidified polymeric membrane having a porous structure; and
- (f) removing the fibrous core from said polymeric membrane, to form a polymeric hollow fiber having a porous tubular membrane wall enclosing an elongated lumen therein.